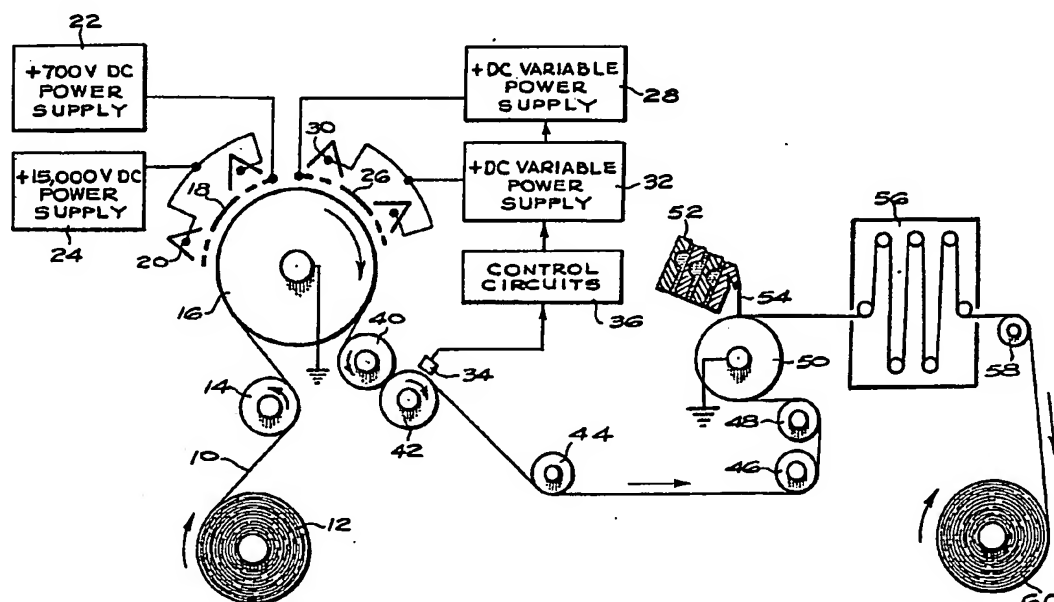




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(21) International Application Number: PCT/US87/03190 (22) International Filing Date: 3 December 1987 (03.12.87) (71) Applicant: EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650 (US). (72) Inventor: HARTMAN, Ronald, L. ; 133 Alcott Road, Rochester, NY 14626 (US). (74) Agent: TURNER, John, B.; 343 State Street, Rochester, NY 14650 (US). (81) Designated States: BE (European patent), CH (Euro- pean patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, NL (European patent).		Published <i>With international search report.</i>

(54) Title: HIGH SPEED CURTAIN COATING PROCESS AND APPARATUS



(57) Abstract

In a process of curtain coating, the use of very high coating speeds is facilitated by application to the surface of the object to be coated of a predetermined high level of electrostatic polar charge. The level of charge which is effective to promote the desired uniformity of coating with minimum formation of coating defects is directly related to the coating speed, so that increasingly higher levels of charge are needed as coating speed is increased. The process is particularly useful for coating photographic materials, such as multi-layer photographic films and papers.

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HIGH SPEED CURTAIN COATING PROCESS AND APPARATUSField of the Invention

This invention relates in general to the process of curtain coating and in particular to the use of curtain coating in the manufacture of photographic materials such as photographic films and papers. More specifically, this invention relates to an improved curtain coating process which is especially adapted to high speed manufacturing operations that are capable of achieving the high degree of precision that is essential in the photographic field, and to apparatus for use in such process.

Background of the Invention

Among the many known methods of coating photographic materials there are two which meet the extreme requirements of the photographic industry for coating uniformity, extreme thinness of layers, wide range in coating speed and especially the ability of applying a plurality of layers simultaneously. The first method known as bead coating is described in Beguin in United States Patent No. 2,681,294 issued June 15, 1954 and in Russell, United States Patent No. 2,761,791 issued September 4, 1956. The latter patent pertains specifically to multi-layer coating in which two or more layers of coating composition are simultaneously applied to a moving support in the manufacture of photographic materials. The second method, known as curtain coating, is described in Greiller, United States Patent No. 3,632,374 issued January 4, 1972 and Hughes, United States Patent No. 3,508,947 issued April 28, 1970. The latter patent specifically pertains to a method of multi-layer curtain coating in which two or more layers of coating composition are simultaneously applied to a moving support by a free-falling curtain in the manufacture of photographic materials.

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The curtain coating method in particular has many advantages in the manufacture of photographic materials that require the application of coated layers of a precise thickness, with regard to both widthwise and lengthwise uniformity, onto a continuously moving support material. It is recognized that many of the advantages achieved by the curtain coating method result from the fact that the free-falling curtain can be formed by a slide hopper which is not in close proximity to the application locus on the moving support. The bead coating process continues to be in general use because it had become so highly developed before the advent of curtain coating in the manufacture of photographic materials. Investigation of bead coating for coating photographic materials was particularly directed to the coating zone where it was found that in order to establish an extremely stable process it was necessary to control two stabilizing forces which effected bead formation. Control and stabilization of the bead formation permitted the use of a wide latitude of coating speeds, layer viscosities and layer thicknesses. The stabilizing forces are first, a pressure differential (suction) applied across the coating bead at the application locus as disclosed in Beguin U. S. 2,681,294 and, secondly, an electrostatic charge differential applied just prior to the application locus as described in Nadeau, United States Patent No. 2,952,559 issued September 13, 1960. Thus, both a pressure differential and an electrostatic charge serve to hold the bead within the coating zone. In a bead coating process, forces which act toward the web, such as those provided by a pressure differential or an electrostatic charge, aid in stabilizing the bead and maintain it in wetting contact with the moving web. In a curtain coating process, however, no bead is ever

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formed and the mechanism of the coating action is distinctly different. Thus, for example, in a curtain coating process, the curtain is free-falling and impinges on the moving support with considerable momentum to provide a sufficient force to stabilize the application locus and insure a uniform wetting line on the moving support. The required momentum is obtained by appropriate selection of the curtain flow rate and the height of free fall.

10 The preferred method for obtaining a uniform electrostatic force at the coating application point in bead coating is to form a bound polar charge on the support at a uniform level. With a bound charge there are equal and opposite electrostatic charges on the two
15 surfaces of the support. To retain the charge on the support until the coating application locus is reached requires that the support be a dielectric material having a very high resistivity. As the charged support passes over the grounded coating roll, the side of the
20 support adjacent to the coating roll mirrors a charge on the coating roll surface which effectively neutralizes the charge on the support in contact with the coating roll surface and creates the equivalent of a net charge on the surface of the support being coated. This
25 creates an electrostatic field at the coating application locus between the surface of the support and the grounded hopper lip. When a moving support with a net charge on the surface to be coated is passed over a grounded coating roller the electrostatic field of the
30 charge is effectively neutralized by the charge mirrored on the grounded coating roll surface.

It is extremely difficult, however, to obtain a uniform electrostatic field at the coating application locus and all subsequent patent disclosures since the
35 disclosure of U.S. 2,952,559 are concerned with the

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effects of combining suction and electrostatic polar charge forces. Attention is directed, for example, to U. S. 3,206,323. Other patents mention use of polar charge assist in the bead coating of photographic materials at significantly lower coating speeds. These include U. S. Patent 3,470,417, U. S. Patent 3,670,203, and U. S. Patent 3,671,806. In addition, other patents disclose methods of measuring and controlling the electrostatic field so that a uniform charge of the required magnitude is obtained. These include U.S. Patent 3,531,314, U.S. Patent 3,730,753, U. S. Patent 3,702,258, U.S. Patent 3,757,163 and U.S. Patent 3,549,406.

As discussed briefly above, the coating mechanisms involved in bead and curtain coating are completely different. Besides the difference in forces used to stabilize the coating at the application locus, the effects of such coating variables as viscosity of the coating composition, flow rate per unit width of coating, and support surface smoothness are usually completely different in a bead coating versus a curtain coating process. With bead coating, to increase the coating speed without affecting coating uniformity, the viscosity of the bottom layer must be reduced (by dilution) thereby increasing the wet coverage as disclosed in U.S. Patent 4,001,024. Also, a rough support surface such as a textured or matte surface becomes much more difficult to coat at high speeds. In all of these cases, when the coating speed is increased, the coating bead has a greater tendency to either break or become unstable, resulting in cross lines in the coating or extensive entrainment of air bubbles in the coating at the support-coating interface. With a curtain coating process, just the opposite relationships to the above noted bead coating relationships are observed. When curtain coating failures occur at high coating speeds they can often be avoided by

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increasing the viscosity of the coating composition, or lowering the wet coverage of the bottom layer or coating a rough support. On the other hand, when curtain coating at high speeds, a high flow rate per unit width can often
5 result in the problem of "puddling" of the coating on the support, which commonly occurs when the curtain velocity at the application locus on the support is greater than the velocity of the support being coated. However
10 puddling can also occur when the support velocity is greater than the curtain velocity. Thus coating failure at high coating speeds seems to occur because the momentum of the curtain at the coating application locus is too high.

In view of these directly conflicting
15 requirements resulting from radically different coating mechanisms involved in bead coating and curtain coating processes, it is indeed surprising that establishing a high level of an electrostatic polar charge on the surface of a support could achieve unexpected advantages in
20 curtain coating. While the use of a low level electrostatic field was well known and developed for the bead coating process, there was no recognition in the prior art that it might be useful in solving the problems that arise in high speed curtain coating of photographic
25 materials. On the contrary, it was believed that such a force would be of no benefit whenever there was adequate curtain momentum. The observed failure of curtain coating at high speeds seemed to occur because there was too much curtain coating momentum so applying an electrostatic
30 force at the coating application locus would if anything have been expected to make the situation worse. Such a force might possibly have been considered useful at low coating speeds when there was insufficient curtain momentum, but not when the curtain momentum was more than
35 adequate.

While the applicant does not wish to be bound by any theoretical explanation of the manner in which his invention functions, it is believed that the electrostatic polar charge provides an attraction between the falling curtain and the support which is sufficiently strong to provide a uniform and defect free coating.

It is postulated that the coating defects encountered in curtain coating as the web speed is increased to very high levels result in part from the mechanism referred to herein as "insufficient viscous friction" force. The effect of "insufficient viscous friction" force is characterized by a defect which results from a multitude of entrained air bubbles between the coating and the support and the presence of longitudinal bands which result when droplets of coating composition form upstream of the application locus and coat out to provide such bands. The "insufficient viscous friction" force hypothesis is suggested by the inability to coat uniformly, because the coating solution viscosity is too low, the flow rate is too high, or the support surface is too smooth. The problems resulting from "insufficient viscous friction" force manifest themselves in curtain coating only at very high coating speeds such as at web speeds of about 250 centimeters per second or higher. In accordance with this invention, a predetermined high level of electrostatic polar charge is utilized to solve these problems in high speed curtain coating, as contrasted with known use of electrostatic polar charge in bead coating, which involves a distinctly different purpose, namely the purpose of stabilizing a coating bead. A high level of electrostatic polar charge apparently contributes a substantial attractive force which acts, in the appropriate direction, in the region where the curtain impacts the web, and thereby substantially increases the speed at which coatings can be successfully applied by the

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The following examples further illustrate the invention.

EXAMPLE I - By the bead coating method:

A multiple slide bead coating hopper similar to that shown in U. S. 2,761,791 was used except that the hopper was set up to coat 7 layers simultaneously. The product coated was Ektacolor Paper which contains 7 separate layers. The wet thickness and viscosity of the 7 layers are tabulated in Table I.

10

Table I

<u>Layer</u>	<u>Wet Coverage Microns</u>	<u>Viscosity Centipoise</u>
Blue Sensitive (Bottom)	32 or 37	6.5 or 4.6
15 Interlayer	5	115
Green Sensitive	15	50
Ultraviolet Filter	7	63
20 Red Sensitive	14	32
Ultraviolet Filter	7	63
Overcoat	7	93

The viscosity of the bottom layer was adjusted by dilution with water in order to obtain satisfactory coatability. Satisfactory coatability is defined as a stable coating system which is free of mottle, crosslines, micro bubbles and other coating defects. It was desired to attempt to coat this product at high speed (400 cm/sec or higher) Table II shows the maximum coating speed achieved as a function of bottom layer viscosity and polar charge voltage. Both Matte (rough) surface and Glossy (smooth) surface supports were used as indicated in Table II.

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Table II (Bead Coating Method)

Support Surface	(Maximum Coating Speed cm/sec)			
	No Polar Charge		350 Volts Polar Charge	
	Bottom Layer		Bottom Layer	
	Viscosity		Viscosity	
	I (a)	I (b)	I (c)	I (d)
5	6.5 cps	4.6 cps	6.5 cps	4.6 cps
Matte	300 cm/sec	350 cm/sec	350 cm/sec	400 cm/sec
Glossy	350 cm/sec	400 cm/sec	400 cm/sec	**

10 ** Polar charge not required to coat at 400 cm/sec.

For the matte surface support dilution of the bottom layer from 6.5 to 4.6 centipoise illustrated in Examples I(a) and I(b) resulted in an increase in maximum coating speed from 300 to 350 cm/sec while for a glossy surface the increase was from 350 to 400 cm/sec. When a polar charge of 350 volts was applied to the support prior to the coating zone as illustrated in Examples I(c) and I(d) the maximum coating speed for the matte surface support increased 50 centimeter/sec to a maximum of 400 centimeters/sec for the very dilute bottom layer. This amounts to an improved maximum coating speed of approximately 14% to 17% depending upon the viscosity of the bottom layer when used with a matte surface. Application of a higher level of polar charge above 350 volts was found not to appreciably improve bead coating speed.

For the glossy surface support a polar charge was not required to achieve satisfactory coatability at a speed greater than 400 cm/sec. Note that the glossy surface support can generally be coated at approximately 50 cm/sec greater speed than the matte surface. Dilution of the bottom layer from 6.5 to 4.6 centipoise increased the maximum coating speed by 50 cm/sec for both types of supports.

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It is well known that one of the advantages of using the curtain coating method for coating photographic materials over the known bead coating method is that the bottom layer does not have to be more dilute than the other layers. This is in contrast to the need in bead coating to use a very dilute bottom layer. In the above example 40% of the total water is in the bottom layer. This requirement tends to limit the speed at which a continuous coated web support can be dried. While the lowermost layer in a bead coating process is usually 10 centipoise or less and preferably 3 to 5 centipoise, the outer layers of a stable free falling curtain usually are 40 centipoise or higher. The advantages of coating with higher viscosity coating compositions are well known and discussed in Hughes U.S. Patent 3,508,947 one advantage being the significant decrease in the water load requirements on the drier which must continuously and uniformly dry the delicate photographic coating.

EXAMPLE II - Curtain Coating Method

A multiple slide curtain coating hopper similar to that shown in Figure 1 of U.S. Patent No. 3,508,947 was used except that the hopper was set up to coat 7 layers of coating compositions simultaneously. All layer viscosities and wet coverages except for the bottom (blue sensitive) layer were identical to those shown in Table I. The bottom (blue sensitive) layer was replaced with a coating composition having a viscosity of 26 centipoise with a wet coverage of 20 microns. The coating speed obtained using a matte and a glossy support surface are tabulated in Table III.

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Table III (Curtain Coating Method)

Bottom Layer Viscosity 26 centipoise, wet coverage 20
microns

	Maximum Coating Speed cm/sec)	
	<u>No Polar Charge</u>	<u>700 Volts Polar Charge</u>
5		
	<u>Support Surface</u>	
	Matte	400 cm/sec **
	Glossy	300 At least 500 cm/sec

10

** Polar charge not required to coat at 400 cm/sec.

15 The matte surface curtain coating data recorded
in Table III should be compared with the matte surface
bead coating data recorded in Table II. Whereas with
bead coating it was necessary to use a polar charge of
350 volts to coat at a maximum speed of 400 cm/sec it
was shown that such a speed could be achieved with the
curtain coating method without the use of polar charge
20 assist.

The coating requirements for a glossy surface
support however were found to differ significantly and
therefore could not be predicted based on prior
knowledge of the bead coating method. For example,
25 Table III shows that a maximum coating speed of only 300
cm/sec could be achieved for a glossy surface support
using a 26 centipoise bottom layer when no polar charge
assist was used. Table II relating to the bead coating
method shows that for a glossy surface a maximum coating
30 speed of 400 cm/sec could be achieved without use of a
polar charge.

When a polar charge of 700 volts was applied to
the coating surface prior to the application point the
glossy surface support could be curtain coated at a
35 speed of at least 500 cm/sec. This amounts to an

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increase in the achievable curtain coating speed for the glossy support surface of at least 67% over that obtainable when no polar charge was used. Coating at higher speeds is possible when increasingly higher

5 levels of polar charge are used as shown in Figure 2.

Comparison of these examples shows that coating of photographic materials using the bead coating method which requires a very dilute (low viscosity) bottom layer has an upper limit for coating speed of about 400
10 cm/sec.

When coating a photographic material using the curtain coating process it was unexpectedly found that much higher coating speeds were possible. Although a very concentrated (higher viscosity) bottom layer is
15 applied when using the curtain coating it was unexpectedly found that application of a very high level of polar charge to coat a smooth web support such as a glossy support would result in coating speed well above 400 cm/sec.

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What is claimed

1. In a process of coating an object with liquid coating composition in which said object is advanced along a path through a coating zone, and a
5 free-falling curtain which is comprised of one or more layers of liquid coating composition and extends transversely of said path is impinged within said coating zone on a surface of said moving object to form thereon a coating comprised of one or more layers; the
10 improvement which comprises establishing an electrostatic polar charge on the surface of said object to which said coating is applied, the magnitude of said charge being sufficient to insure the uniformity of said coating.
- 15 2. In a process of coating an object with liquid coating composition in which said object is advanced along a path through a coating zone, and a free-falling curtain which is comprised of one or more
20 layers of liquid coating composition and extends transversely of said path is impinged within said coating zone on a surface of said moving object to form thereon a coating comprised of one or more layers; the improvement which comprises advancing said object at a
25 speed of at least 250 centimeters per second and establishing an electrostatic polar charge on the surface of said object to which said coating is applied, the magnitude of said charge being selected in
30 accordance with the speed of said object so that the ratio of said charge at any point on said surface, measured in volts, to said speed, measured in
centimeters per second, is at least 1 to 1.
3. In a process for the manufacture of a photographic element in which a web is advanced along a
35 path through a coating zone and a free-falling curtain which is comprised of a single layer of liquid

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photographic coating composition and extends transversely of said path is impinged within said coating zone on said web to form a coating thereon; the improvement which comprises establishing an

5 electrostatic polar charge, of a magnitude sufficient to enhance the uniformity of said coating, on the surface of said web to which said coating is applied.

4. In a process for the manufacture of a photographic element in which a web is advanced along a

10 path through a coating zone and a free-falling curtain which is comprised of a single layer of liquid photographic coating composition and extends transversely of said path is impinged within said coating zone on said web to form a coating thereon, the

15 improvement which comprises advancing said web at a speed of at least 400 centimeters per second and establishing an electrostatic polar charge on the surface of said web to which said coating is applied, the magnitude of said charge being selected in

20 accordance with the speed of said web so that the ratio of said charge at any point on said surface, measured in volts, to said speed, measured in centimeters per second, is at least 1 to 1.

5. In a process for the manufacture of a

25 photographic element in which a web is advanced along a path through a coating zone and a free-falling curtain which is comprised of a plurality of layers of liquid photographic coating composition and extends transversely of said path is impinged within said

30 coating zone on said web to form a multi-layer coating thereon; the improvement which comprises establishing an electrostatic polar charge, of a magnitude sufficient to enhance the uniformity of said multi-layer coating, on the surface of said web to which said coating is applied.

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6. The process as claimed in claim 5 in which said web is passed around a coating roll of lesser width than the width of said web so that said web overhangs said coating roll and the electrostatic polar charge which is established on said web is of greater magnitude over the regions of said web surface which overhang said coating roll than over the remainder of said web surface.

7. In a process for the manufacture of a photographic element in which a web is advanced along a path through a coating zone and a free-falling curtain which is comprised of a plurality of layers of liquid photographic coating composition and extends transversely of said path is impinged within said coating zone on said web to form a multi-layer coating thereon, the improvement which comprises advancing said web at a speed of at least 400 centimeters per second and establishing an electrostatic polar charge on the surface of said web to which said multi-layer coating is applied, the magnitude of said charge being selected in accordance with the speed of said web so that the ratio of said charge at any point on said surface, measured in volts, to said speed, measured in centimeters per second, is at least 1 to 1.

8. The process as claimed in claim 7 wherein said web is composed of cellulose acetate film.

9. The process as claimed in claim 7 wherein said web is composed of polyethylene terephthalate film.

10. The process as claimed in claim 7 wherein said web is composed of polyethylene-coated paper.

11. The process as claimed in claim 7 wherein at least one of said layers is composed of a gelatin silver halide photographic emulsion.

12. The process as claimed in claim 7 wherein the magnitude of said charge, measured in volts, is at least equal to the speed of said web, measured in centimeters per second, plus one hundred.

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13. Curtain coating apparatus comprising:
means for advancing an object to be coated
along a path through a coating zone;
means for forming a free-falling curtain
5 comprised of one or more layers of liquid coating
composition which extends transversely of said path and
impinges within said coating zone on a surface of said
moving object to form thereon a coating comprised of one
or more layers; and
10 means for establishing an electrostatic
polar charge of a magnitude sufficient to enhance the
uniformity of said coating, on the surface of said
object to which said coating is applied.
14. Curtain coating apparatus as claimed in
15 claim 13 wherein said advancing means is capable of
advancing said object at a speed of at least 250
centimeters per second and said charge establishing
means is capable of establishing a electrostatic polar
charge of a magnitude such that the ratio of said
20 charge, measured in volts, to said speed, measured in
centimeters per second, is at least 1 to 1.
15. Curtain coating apparatus as claimed in
claim 14 wherein said object is a web and said means for
advancing said object is a web conveyance system capable
25 of operating at a controlled preselected speed.
16. Curtain coating apparatus as claimed in
claim 14 wherein the electrostatic charge is a bound or
polar charge said means for establishing an
electrostatic polar charge comprises a rounded backing
30 roll and at least one grid-controlled ionizer.
17. Curtain coating apparatus as claimed in
claim 14 wherein said means for forming a free-falling
curtain comprises a multiple-slide hopper.

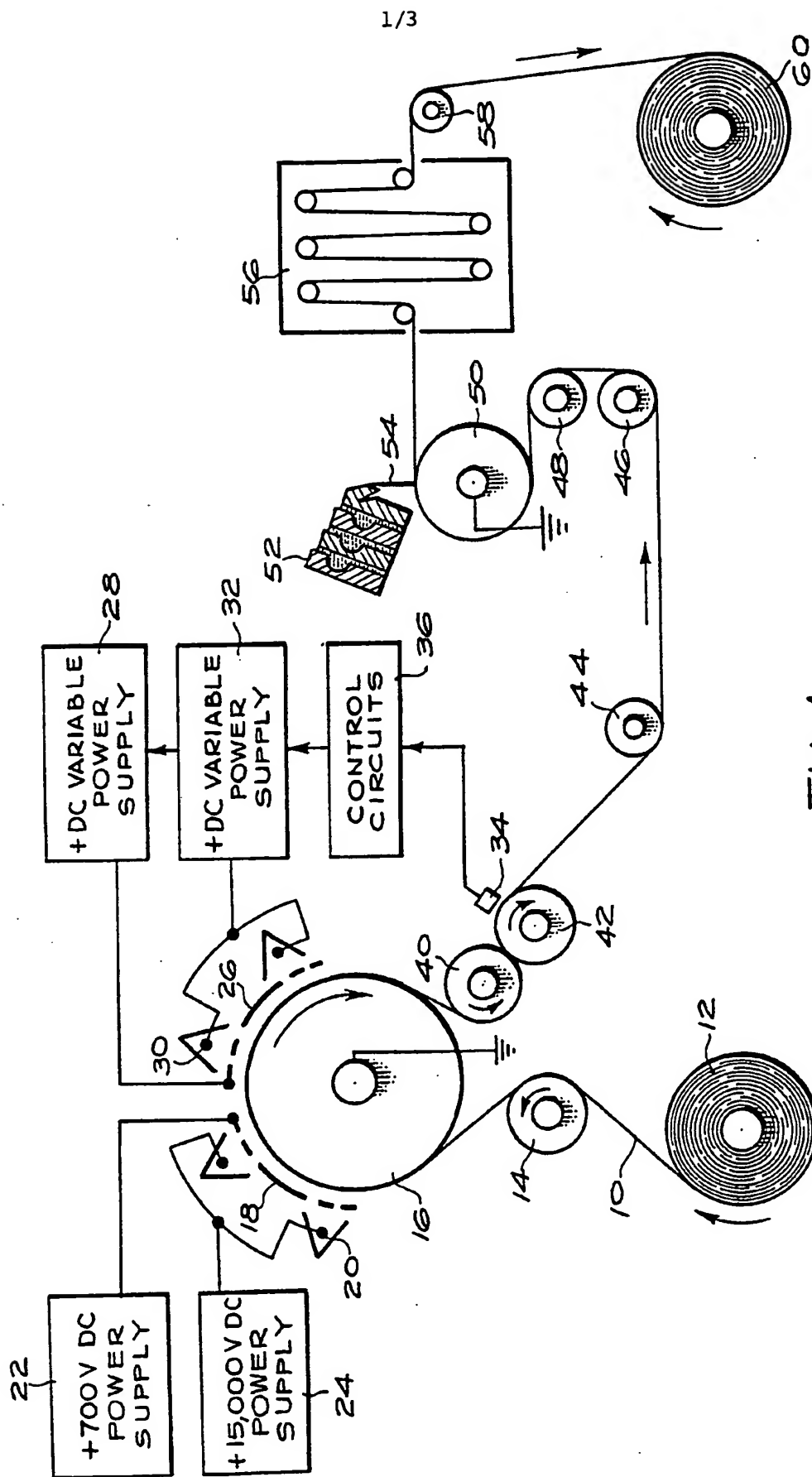


Fig. 1

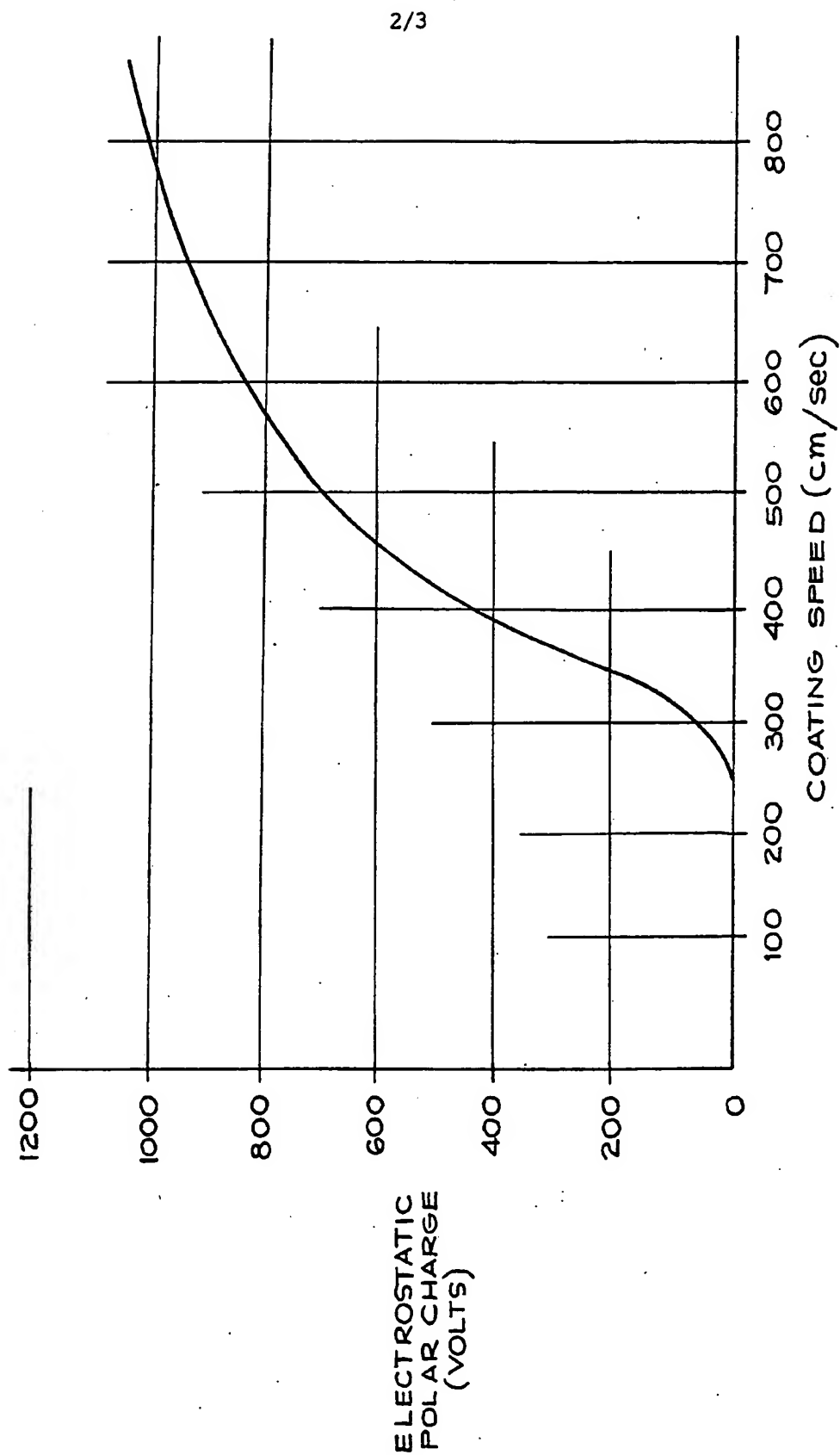


Fig. 2

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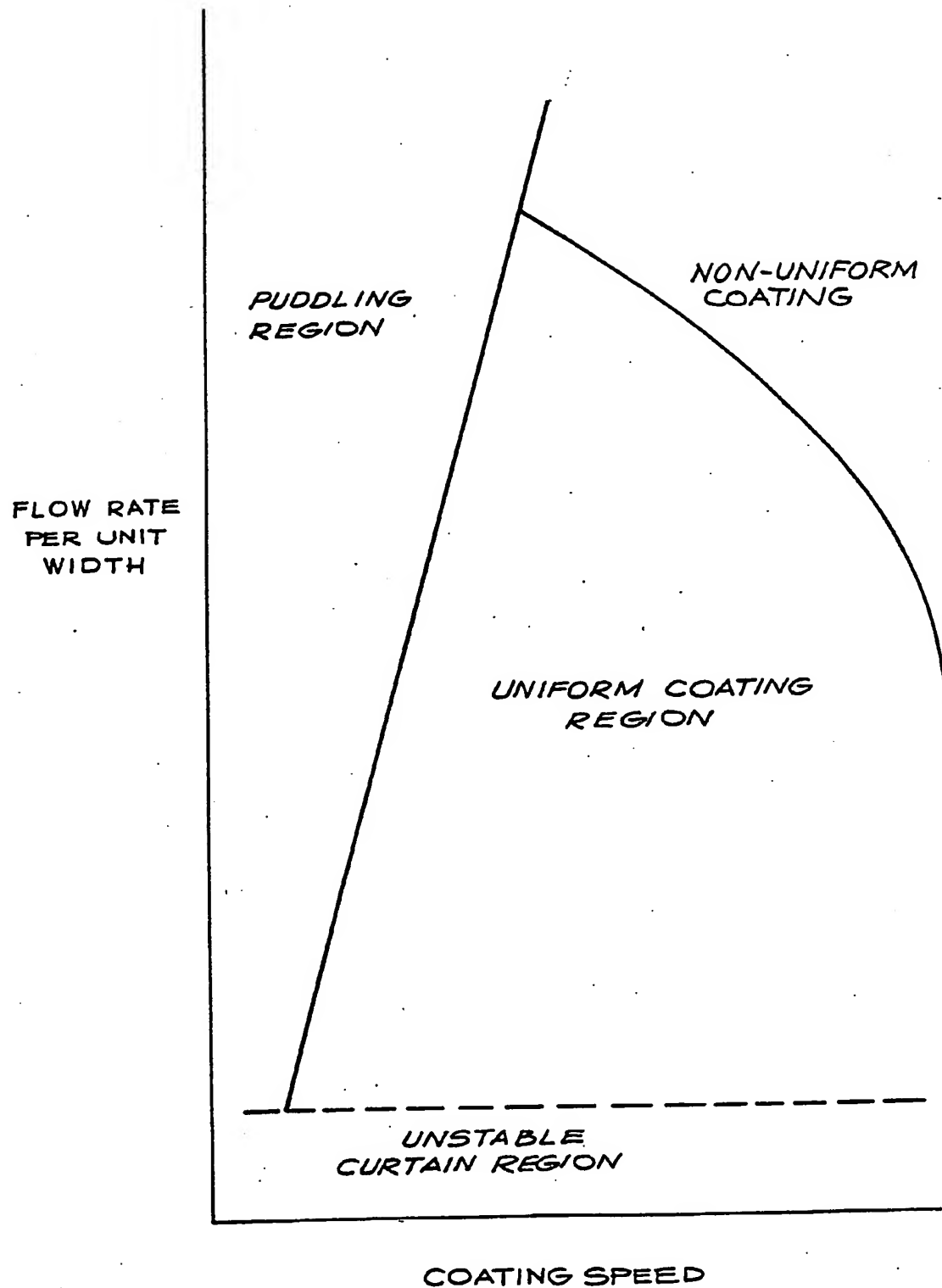
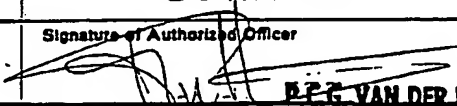


Fig. 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 87/03190

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : G 03 C 1/74; B 05 D 3/14; H 05 F 3/04		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
IPC ⁴	G 03 C 1/74; B 05 D 3/14; H 05 F 3/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X,Y	EP, A, 0136606 (POLAROID) 10 April 1985, see the whole document --	1-17
Y	US, A, 3757163 (C.B. GIBBONS et al.) 4 September 1973, see figures 1,2 cited in the application --	1-17
Y	Patent Abstracts of Japan, vol. 10, no. 366 (C-390)(2423), 6 December 1986 & JP, A, 61161117 (FUJI PHOTO FILM CO LTD) 21 July 1986 --	1-17
Y	GB, A, 1166500 (FUJI PHOTO) 8 October 1969, see page 2, lines 38-48; claims --	1-17
Y	US, A, 3462286 (W.F. DE GEEST et al.) 19 August 1969, see column 3, lines 55-63 --	1-17
A	EP, A, 0055983 (POLAROID) 14 July 1982, see abstract --	1
A	FR, A, 1517840 (FUJI) 22 March 1968, see example 1 -----	1-17
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
28th July 1988		26 AUG 1988
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		 P. G. VAN DER PUTTEN

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8703190

SA 19929

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 18/08/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0136606	10-04-85	US-A- 4517143 JP-A- 60095899 CA-A- 1230372	14-05-85 29-05-85 15-12-87
US-A- 3757163	04-09-73	None	
GB-A- 1166500	08-10-69	DE-A,B 1577745 FR-A- 1517840	30-04-70
US-A- 3462286	19-08-69	None	
EP-A- 0055983	14-07-82	JP-A- 57167750 US-A- 4457256 CA-A- 1178134	15-10-82 03-07-84 20-11-84
FR-A- 1517840		GB-A- 1166500 DE-A,B 1577745	08-10-69 30-04-70